4 Geobotanical and Biogeochemical Prospecting for Heavy Metal Deposits in Europe and Africa

Wilfried Hans Otto Ernst

4.1 Introduction

The use of plants and vegetation as a guide to find exploitable orebodies has a long history. In ancient times people certainly have recognized a relationship between plant and soil. The first written report on an indicator plant, i.e., a plant with a high affinity to an environmental factor, was presented by Thalius in 1588 [1]. From a number of plant species, composing the heavy metal vegetation in the Harz mountains [2], he selected *Minuartia verna* as an indicator of ore veins. This member of the Caryophyllaceae was later recognized as a very useful indicator of metal-enriched soils throughout Europe [3]; still new sites on metal outcrops are associated with this plant species [4].

In the same century, when Thalius published his flora, Agricola [5] adviced ore prospectors to consider abnormalities of plants or vegetation: "Likewise along a course where a vein extends, there grows a certain herb or fungus which is absent from the adjacent space, or sometimes even from the neighbourhood of the veins" [5, book 2].

It lasted nearly 300 years, to appreciate geobotanical prospecting once more when Henwood [6] mentioned the use of *Armeria maritima* as copper indicator on a copper enriched bog at Dolfrwynog (Wales). This indicator plant is a wonderful example of misinterpretation, misunderstanding and ignorance of literature: First of all, Antonovics and coworkers [7], working at Bangor (Wales) at that time, located Dolfrwynog not in Wales, but in Scotland. Secondly, Brooks [8] judged on this indicator plant: "The reputation of this plant is based only on this obscure paper in which Henwood himself quoted the opinion of the local people." Both authors ignored the rediscovery of this site by Ernst [9, 10] and a first analysis of the copper concentrations of this bog. The rediscovery was the start of a publication wave devoted to the biogeochemistry of this site [11 – 15].

Lack of adequate recognition is obviously still a characteristic feature in biogeochemical prospecting [15], because it is obviously difficult to integrate three academic disciplines – geobotany, geochemistry and geology. Therefore the purpose of this chapter is to elaborate possibilities and impossibilities of plants in their role in geobotanical and biogeochemical prospecting for heavy metals.

Conform to biological reaction patterns to a surplus of heavy metals, plants can be classified as *non-reactors* and *reactors* (Fig. 1). A non-reacting plant has to be completely insensitive, i.e., the uptake of an excess of heavy metals is completely avoided. Such a system is evolutionary impossible, because ion uptake by plants is not absolutely oriented to only essential elements [17]. Another aspect of a lack of reaction may be caused by the non-availability of a heavy metal to plants. Uptake of heavy metals can only occur from a solution surrounding the plant roots. Thus heavy metals have to be leached from the orevein, and dissolved in the soil moisture. This process is dependent on the exposure of the metal to soil moisture, the acidity of this soil solution, the presence of complexing or adsorbing agents, and the strength of all ions in the soil solution. Therefore, the total concentration of a heavy metal in the bedrock or the overlaying soil is not interesting for all aspects of ore prospecting by biological means. As a consequence, a lot of techniques have been developed to get an impression of metal solubility in soil moisture and of metal availability to plants [18]. All extraction techniques have one drawback: the availability can actively be modified by plants: they can exude H^+-ions to keep electroneutrality and various organic acids due to a shortage of essential nutrients [19].

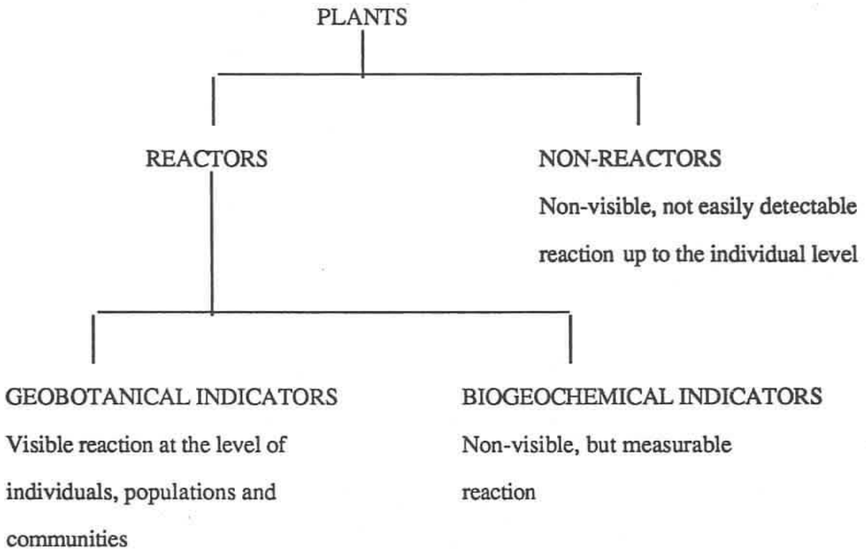
PLANTS
REACTORS
NON-REACTORS
Non-visible, not easily detectable reaction up to the individual level
GEOBOTANICAL INDICATORS
Visible reaction at the level of individuals, populations and communities
BIOGEOCHEMICAL INDICATORS
Non-visible, but measurable reaction

Fig. 1. Reaction types of plants and vegetation on a surplus of heavy metals (modified after Webb and Millman 1951 [16]).

Except in the case of metal insolubility, all plants will be *reactors*. Within the group of reacting plants, we can discriminate between those with visible (=overt, 16) and non-visible (=covert) reactions. Visibility is here defined for the human eye, i.e., at the level of the individual plant, changes in color and growth forms of plant parts or abundance and presence of species. All these aspects will be treated under the heading of geobotanical prospecting. Visualized reactions (airborne multispectral and thermal imagery, [20], change in fluorescence, [21]) will be treated together with changes of the chemical composition of a plant under the heading of biogeochemical prospecting of ore bodies.

4.2 Some General Principles of Biogeochemical Prospecting

In the natural, i.e., undisturbed situation, a local surplus of heavy metals is due to a mineralization of a rock. Around this mineralized zone a more or less steep gradient of metal concentrations is built up [2]. The impact of the metal surplus on plant growth will depend on the available metal concentration in the rock or after weathering in the soil, its interaction with anorganic and organic soil components, i.e., solubility, exchangeability and speciation, on the presence of other mineral elements and on the pH and Eh of the soil.

From the numerous heavy metals, occurring in the earth crust, only four, Fe, Mn, Zn and Cu, are essential for all higher plants. In addition special groups of higher plants demand some more metals for their optimal growth: Ni in Leguminosae, Co in nitrogen-fixing bacteria associated with legumes, V in the ectomycorrhizal fungus *Amanita muscaria* associated with birch [17, 19]. During the evolution of nutrient uptake systems, plants have not developed ion uptake systems, which are specific for all essential heavy metals. In contrast, all heavy metals being present in a soluble form in the root environment maybe taken up. Therefore ore prospection by plant analysis is a useful tool, especially in those areas where an overburden is hiding an ore body or when the soluble metal concentration is too low to injure plant growth by visible symptoms. The importance of this approach in prospecting for mineral deposits has rapidly increased during the last decades due to the development of new analytical methods (AAS, AES) with multielement capability (ICP-MS) [22]. Biogeochemical methods for prospecting have most widely been applied in the former USSR, USA, Canada and Northern Europe; a restricted use is known for Africa and Australia [8, 15, 23].

The efficiency will depend on the ion uptake system of each plant species and genotype, and on the ability of a plant to accumulate the heavy metals in a target organ. Selection of the most useful target plant part in relation to age-dependent or/and season-dependent accumulation processes will increase the success of biogeochemical prospecting.

4.2.1 The Target Plant Part

Therefore the reaction pattern of a plant to a surplus of heavy metals will be related to the handling of the heavy metals by the plant and the affinity of heavy metals to cell compartments. Target organs can principally be all plant parts, i.e. roots, shoots, leaves, flowers and fruits. Within a plant part different tissues can accumulate heavy metals to different degrees, such as cortex and xylem of the roots [2, 24], bark and wood of twigs and stems ([25], see Chapters 14 and 28, this volume).

In the case of the presence of open and hidden ore bodies, the first target organ of a plant for heavy metals is the root (Tab. 1). The morphology and physiology

Tab. 1. Target Plant Parts for Heavy Metals

below ground	roots (24-29)	-	high affinity of cellwalls to Pb, Cr (2, 24)
	rhizome		
	bulb (31)		
above ground	trunk	-	outer bark
		-	inner bark
		-	xylem sap (39, 40)
			seasonally limited transport of Zn, Cd, Mn
		-	sap wood
		-	hard wood (37)
	twig (36)	-	bark
		-	wood
	leaves	-	age dependent accumulation (32)
	flowers	-	fruit - seed (35)

of the root is very decisive for a successful prospection. Malyuga [23] was the first, giving an account on the importance of the root morphology for mineral prospection. If an ore body is hidden by overburden, but remains still in the root zone, then metals can be brought up to the above-ground plant parts and after their death these metals will accumulate in the upper soil horizon of the overburden. Thus, the root depth of plant species is an important plant character: up to 30 m root depth is not unusual for perennial plants in semi-arid areas. On the other hand, annual plant species with small roots will only be able to indicate ore bodies near the surface. When the heavy metal is accumulated in the roots and not translocated to the shoot, only chemical analysis may let detect the surplus of metals. The root as target for metal accumulation is very relevant for metals with a high affinity to the pectinates in the cell wall, e.g. Cr and Pb [24]. Therefore, high concentrations of these metals in aerial plant parts are very scarce, so that they are nearly no hyperaccumulators, i.e., plant species with a metal concentration in leaves >1000 µg Cr or Pb per g dry wt [26]. Heavy metals with a strong tendency for accumulation in the vacuole [2] are translocated very fast to the shoot, although the translocation is more rapid in metal-sensitive than in metal-tolerant plants (Zn: 27; Cu: 28). A special problem in chemical analysis of roots is their contamination by soil particles; therefore roots have to be carefully cleaned to get reliable analytical data [29].

Other plant parts, growing below soil surface are bulbs and rhizomes. Both are associated with the upper soil layer and therefore only suitable for biomonitoring a soil depth up to 1 m. Although plant species with bulbs and rhizomes can make up a reasonable portion of the vegetation in Africa, also on ore outcrops [30], they are for another reason not promising for biogeochemical monitoring: The metal concentration in bulbs maybe often low because the leaves have a relatively high turnover. Up to now, the only exception are the bulbs of *Merendera filifolia* on a zinc mine in Morocco [31]. However, in this case soil particles may have contaminated the outer decaying leaves.

Once translocated to the *aerial parts of the plants*, heavy metals can be distributed over various organs and within an organ over various tissues. Due to the deciduous character of leaves, the relatively easy way of their sampling and handling in homogenation processes, and their high metal accumulation brought leaves to a favorite position in biogeochemical prospecting. A lot of prospecting can be made more efficient, if leaf age is recognized as important modifying factor of metal accumulation [32]. In rosette plants, the outest leaves are the oldest of the plant and contain the highest metal concentration [25, 33]. In non-rosette, there is an age-gradient along the shoot; the leaves at the bottom of the shoot are generally the oldest, at the top the youngest. In coniferous trees there may be a lot of age-classes of needles on a twig, dependent on plant species and genotypes within a species [25]. In plants with leaves, being shed within a year or a rainy season, all leaves of a plant may be even-aged. In this case, sampling ha~~ve~~ to be delayed and done just before shedding to that the metal accumulation is at maximum [32]. The maximum accumulation is only realized if the heavy metal is present in the soil solution in high concentration, as demonstrated for iron and zinc in a leaf-age gradient of *Agrostis capillaris* (Tab. 2). At the same sampling site, species-specific differences can be demonstrated. Senescent leaves of birch *(Betula pendula)* have

Tab. 2. Concentrations of Some Heavy Metals (μmol g^{-1} dry wt) in a Herb *(Thlaspi coerulescens)*, a Grass *(Agrostis capillaris)* and a Tree *(Betula pendula)* from Mineralized Site at Bergsbø, Sweden. Collection: October 11th, 1988 (Ernst, unpublished data)

	Fe	Mn	Zn	Cu
Thlaspi coerulescens				
mature leaves	4.71	0.79	0.46	0.50
Agrostis capillaris				
decaying leaves	27.61	3.88	16.18	0.34
senescent leaves	25.24	4.05	6.62	0.69
mature leaves	5.81	3.10	6.63	0.34
young leaves	5.22	2.52	4.61	0.30
Betula pendula				
senescent leaves	3.45	3.50	15.42	0.22

twice the zinc concentration that those of *Agrostis capillaris*, but only 14% of the iron concentration and a nearly identical manganese concentration. Therefore, a general chemical survey of the local vegetation should be made in advance of a sampling program, so that the best accumulator species of each element is known.

Due to differences in air humidity and thus transpiration intensity, leaves from the inner canopy of a shrub or tree accumulate less metals than leaves from the outer canopy. In addition, it might be expected that leaves at the top of a tree may be better metal accumulators than those at the bottom. Differences in metal concentration due to leaf position and/or leaf age are governed by the transpiration rate. Most, if not all metals are translocated from root to shoot via xylem transport, often as chemical complexes with organic acids. Transpiration of water by leaves is an important motor of this xylem transport. Therefore a high transpiration rate, caused by moisture deficit of the ambient air, enhances the concentration of the accumulated heavy metals. Holoparasitic plant species, growing in the crown of a tree, such as *Loranthus* and *Viscum* species, have therefore often higher metal concentrations than the leaves of their host plants [34]. The possibility of epiphytic holoparasitic higher plants as targets in biogeochemical prospecting are nearly unexplored.

Flowers are less suitable as target plant parts for metal accumulation, due to their short life period, although their reactivity to heavy metals makes them very good symptomatic indicators [2]. The seasonality of the flowering process demands, however, a good knowledge on the life history of the plants, because the information is only available during a short period of the year. Nevertheless, the accumulation of heavy metals can be high in the reproductive organs compared to vegetative ones (Tab. 3). In the case of *Silene vulgaris* the calix as the most long-lasting part of the reproductive system (from early bud to seed ripeness) has the highest accumulation of those metals being in excess, whereas the capsule, the anthers and the seeds have relatively low metal concentrations [35].

A similar restriction holds for *fruits* although the process of fruit development can last for months, e.g. *Silene vulgaris* 11 to 20 days, hazelnut 6 months, cones of Scotch pine 2–3 years. Up to now, there is no systematic approach for the use of fruits in biogeochemical prospecting. A drawback of such an approach may be the diminished fruit and seed production of plant species on metal-enriched sites.

Twigs and *trunks* are often used in metal prospection [36]. The high morphological differentiation and age gradient within a twig and a trunk demands a careful selection during sampling. Generally the outer bark of a trunk is more enriched by heavy metals than the inner bark. The least accumulation is found in the trunkwood [37]. The metal concentration of a twig is determined by the ratio of bark to wood. Bark production and bark longevity are further modifying factors. The advantage of analyzing bark and twigs versus leaves is their permanent presence throughout the year. Modern sampling techniques, especially of heavily forested areas, e.g. tree-top sampling from a helicopter [38] will certainly stimulate tree bark and twig analysis.

Another parameter of trees, to be used as a tool for biogeochemical prospecting, is the bleeding sap of tree species with a pronounced sap stream. Up to now, only birch trees [39, 40] have been explored with good success in Finland and Russia in zinc prospection. The advantage is a shortening of the time-consuming procedure of sample preparation, a disadvantage is the short period of oozing.

4.2.2 Relationship between Metals in the Environment and in the Plant

The demonstrated diversity of target plant parts, the different affinity of heavy metals to cell compartments and via translocation to plant parts and plant tissues, the competition of chemical elements for the same uptake system, e.g. phosphate and arsenate [41], and the complex relationship between total metal concentration and metal solubility, all these aspects together ~~may it~~ make plausible that linear relationships between metal concentrations in the root environment and in the plant are more the exception [42] than the rule [43]. In addition, shedding plant parts with metabolically complexed metals will change the metal speciation in the environment and its uptake by plants [44].

A high accumulation of heavy metals by a plant species will demand such a metabolic regulation, that metals cannot affect the normal metabolism as long as the metal does not cause visible symptoms. One of the unsolved problems is the high diversity of metal demands among genotypes of a species [2, 28], between taxonomically related species of the same genus, and between higher taxonomic ranks. Superposed on this demand is the ability of metal accumulation. The classification of plants as excluders or hyperaccumulators are nothing more than the elaboration of extreme accumulation patterns. The limit set for a hyperaccumulator is abritarily, especially if the element concentration is judged as μg per g dry wt, and not on its physiological activity as μmol per g dry wt (Tab. 4). The comparison

Tab. 3. Metal Accumulation in Reproductive Plant Parts of *Silene vulgaris*, Collected on a Zinc Mine at Blankenrode in Comparison to Mature Leaves ([35], Ernst, unpublished data)

Plant part	Fe	Mn	Zn	Cu	Cd	Pb
Vegetative						
mature leaves	9.64	0.83	21.60	0.10	0.15	0.51
Reproductive						
anthers	7.96	0.44	2.26	0.20	0.02	0.06
calyx (fruiting)	10.00	0.72	16.68	0.08	0.07	0.42
capsule	4.84	0.49	8.65	0.10	0.06	0.08
seed	0.87	0.47	1.71	0.06	0.04	0.01

Tab. 4. Threshold of Heavy Metals in Hyperaccumulators in an Analytical and a Physiological View

Element	Analytical view (26) ($\mu g\ g^{-1}$ dry wt)	Molecular equivalent ($\mu mol\ g^{-1}$ dry wt)	Physiological equivalent and target plant part ($\mu mol\ g^{-1}$ dry wt)
Au	1	0.005	> 0.1 (roots)
Co	1000	16.97	15 (leaf)
Cu	1000	15.74	15 (leaf)
Cr	1000	19.23	>15 (roots)
Ni	1000	17.32	15 (leaf)
Pb	1000	4.83	15 (roots)
Mn	10000	182.02	150 (leaf)
Zn	10000	152.98	150 (leaf)

in Tab. 4 demonstrates that a threshold of 1000 $\mu g\ g^{-1}$ of Pb is a four times lower physiological equivalent than 1000 $\mu g\ g^{-1}$ of Cr. As long as these classifications are not accompanied with a precise description of the analyzed plant part and its physiological state, they are good examples for the Guinness book of records, but they will not be helpful in highlighting the metal plant-soil relationship. The accumulation of a heavy metal in the leaves, depends on the translocation from the root to the shoot; therefore less mobile elements (Cr, Pb) will be accumulated in the root, resulting in a root hyperaccumulator. In such species the leaves may even indicate metal excluders *sensu* Baker [27].

4.3 Geobotanical Prospecting

Long term exposure to high metal concentrations will initiate a selection process among the various plant species of a vegetation. The intensity of the stress, i.e., metal availability to the plants, will determine the degree of selection. Due to the various target plant parts and the differences in metal uptake and metal accumulation the selection process may eliminate certain plant species from an existing vegetation (this aspect is typical for anthropogenic metal surplus, see Chapter 14, this volume). In the undisturbed situation, species elimination will only take place if due to erosion processes, the vegetation growing on an overburden is more and more exposed to increasing metal concentration or to seepage with metal-enriched water. In such situations, the selection will take place at the time of invasion, when the seed germinate and the seedling has to establish and grow to maturity.

4.3.1 The Effect Concentration

As soon as a heavy metal is taken up by a plant, it will cause reactions in the cellular metabolism. The degree of the reaction will depend on its role in the metabolism, the possible substitution by another element, and the concentration of the heavy metal. With regard to a visible reaction of the plant on the metal concentration, the metabolism has to be disturbed. This disturbance can be caused by a shortage or a surplus of an element (Fig. 2). A shortage of an element in the case of the vicinity of ore bodies can be caused by an imbalance of the soil solution. A well-known reaction is the iron and manganese chlorosis at high concentrations of zinc or copper, which hamper the uptake of sufficient amount of iron and/or manganese (Tab. 5) by the plant [2]. A similar aspect is the competition of arsenate and phosphate uptake system [41]. In this latter case the plants have a shortage of phosphorus, which stimulates the synthesis of red plant pigments, the anthocyanins, so that finally follow-up reactions can be used for visible prospecting.

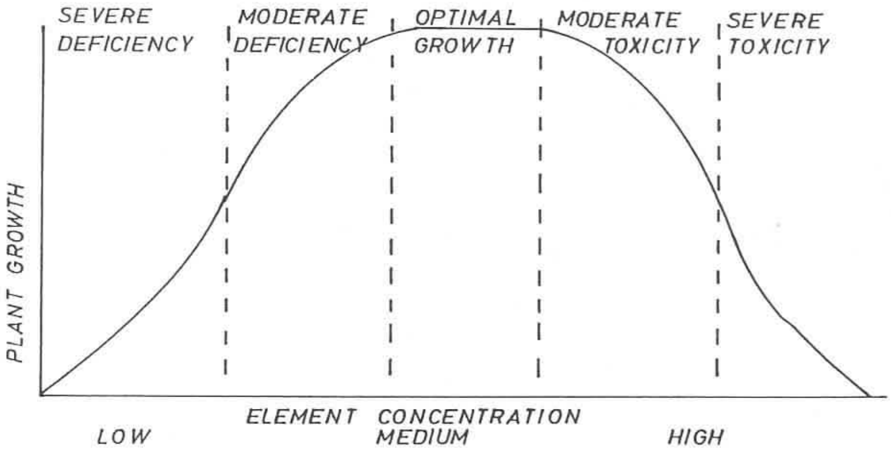

Fig. 2. The reaction of a plant on shortage, adequate and surplus supply of a heavy metal, which is essential in a plant's metabolism.

As long as the metabolism is nearly not disturbed, i.e. around the optimal range, visible deviation of "normal" plant behavior will not be detectable, even if increased concentration of a heavy metal may be detectable by chemical analysis (Fig. 2). As soon as a surplus of the element disturbs the metabolism, reactions will become visible. Once more, it may be a chlorosis, discoloration, a necrosis (brown spots on leaves), stunted growth, or teratological performance of plant parts, when we consider individual plants (symptomatic indication). At the population levels it may be the decrease or increase of the number of individuals or certain genotypes. The presence or absence of certain plant species will change the appearance of the plant community, either by the presence of a specific indicator or by the presence of a specific indicator vegetation. Both processes will be simultaneously accompanied by the disappearance of plant species or life forms, e.g. the absence of trees on sites with a very high metal availability [2].

Tab. 5. Heavy-Metal Concentrations in Green and Chlorotic Leaves of a Herb (*Cardaminopsis halleri*, Cruciferae) and a Grass (*Agrostis capillaris*) on a Seepage Area of a Zinc-Lead Vein in the Elpe Valley in Germany [45]

	Fe	Mn	Zn	Cu	Cd	Pb
Cardaminopsis halleri						
green	3.8	2.3	97.9	0.12	0.08	0.83
chlorotic	2.2	0.5	382.4	0.12	0.50	0.16
Agrostis capillaris						
green	1.4	0.90	6.6	0.15	0.01	0.01
chlorotic	1.4	0.34	17.3	0.12	0.03	0.01

4.3.2 Symptomatic Indicators

As long as the metabolism is only disturbed for a short period of the growing season, a normal growth pattern will develop, as after a *chlorosis* in *Becium homblei* and *Cryptosepalum maraviense* [24, 26] on copper outcrops in Zambia, and after zinc-induced chlorosis in *Agrostis capillaris* and *Cardaminopsis halleri* in Germany [2, 3, 45]. Another form of color change is the discoloration of flowers. Up to now, only the change from normally pink to greenish flowers in *Matthiola fruticulosa* on the Pb–Zn outcrops and mine tailings of Lavrion in Greece are well known [2, 47].

Malformation of plant parts is another reaction to a sublethal concentration of heavy metals. Metal prospectors in the former USSR have widely applied these teratologies for metal prospection. Examples are the dwarfism of *Betula platyphylla*, *Ledum palustre* and other plant species on lead and zinc veins [48], chlorotic dwarf forms of *Pulsatilla patens* on nickel enriched soils at Tuva [23], dwarfed needles of *Picea abies* on a zinc anomaly at Blankenrode (Germany) [25], stunted plant growth with discoloration on a zinc-lead vein at Balsfjord in Norway [49], and dwarfed plants of *Merendera filifolia* on copper-zinc veins in Morocco [31]. Morphological changes of petals are reported from *Papaver macrostomum* in Armenia on soils enriched by Cu, Pb and Zn [50] and from *Symphytum officinale* on uranium anomalies in Poland [51]. Such discoloration and malformation may also be detectable by remote sensing techniques, because digital image analysis can help to distinguish huge individuals or clusters of small individual species [52].

4.3.3 Specific Indicator Plants

High concentrations of heavy metals exert a strong pressure on existing genotypes among a population and on species among a vegetation. Only those genotypes, which can response positively due to their genetic and physiological potential will survive. In first instance, there is no pressure on morphological characters, so that metal-resistant and non-resistant (sensitive) genotypes cannot be distinguished by eye [53 – 55]. Examples of experimentally demonstrated metal-resistance of widely distributed species in Europe are the grasses *Agrostis capillaris (A. tenuis)* [53], *A. stolonifera* [56], *Anthoxanthum odoratum* [57], *Deschampsia caespitosa* [58], *Festuca ovina* [59]; *F. rubra* [60] and the herbs *Silene vulgaris (S. inflata, S. cucubalus)* [61], *S. maritima* [62], *Armeria maritima* s.l. [63] and *Thlaspi goesingense* [64]. In Africa, no common species have been tested for their metal resistance. The grass species *Cynodon dactylon, C. aethiopicus, Dactyloctenium geminatum, Panicum repens, Paspalum vaginatum,* and *Sporobolus virginicus,* however, were shown to be successful colonizers of toxic mine waste. These strong physiologically and genetically differentiated ecotypes are not very useful for prospection tools despite their great advantage in biochemical, physiological, ecological and genetic studies [64a, 64b]. Due to their metal resistance they can endure high metal concentrations without showing visible symptoms.

In addition to these ecotypes of common species, the severity of the selection pressure operating has let come to existence plant species, which are morphologically – often only slightly – different from their obvious ancestors on non-mineralized environments. Such *vicarious* species are frequently described from heavy metal veins in Africa and may have evolved metal-tolerance some thousands or more years ago, i.e., palaeo-endemic species [68]. Some examples from Central Africa are presented in Tab. 6. Wild and Bradshaw [68] and Brooks and Malaisse [69] report a lot of these vicarious species, however, the experimental evidence has not yet been presented. In Europe the numbers of so-called endemic *Alyssum* species on nickel-bearing environment [70], may be examples of the evolution pressure on nickeliferous outcrops; but it is more reasonable to suggest that all these endemics can be reduced to one or two species, if appropriate modern biosystematical and genetic techniques are used. Other species have been taxonomically re-evaluated, so that they are no more separated from their ancestors, e.g., *Thlaspi coerulescens* (J. and C. Presl), which included the metal endemic *Thlaspi calaminare* Lejeune and the fairly wide-spread non-metalliferous *Thlaspi alpestre* Jordan [71].

Another example is the genus *Armeria.* Metal-endemics have been described as *Armeria bottendorfensis* Schulz from a copper outcrop at Bottendorf (Germany) [2, 72a], *Armeria halleri* Wallr. from soils enriched by zinc, lead, copper, thallium, and cadmium from Germany and Poland [2, 73], *Armeria calaminaria* Petri from zinc-lead rich soils in West-Germany and Belgium [2] and *Armeria serpentini* Gauckler [2] from nickel-enriched serpentine in Southern Germany. Although they are genetically distinct in the chemistry of the anthocyanins of their flowers [2], a revision based on morphological traits of these metal-endemics has restricted them to a hybrid swarm between the atlantic *Armeria maritima* (Mill.) Willd. and the continental *A. elongata* Hoffm. [74].

Tab. 6. Vicarious Metal-Resistant Species from Heavy Metal Soils (Metal-Endemics) and their Widely Distributed Relatives from Non-Mineralized Environments in Central Africa

Plant species	Metal resistance
Becium homblei (65, 66)	Cu, Ni
Becium obovatum (65, 66)	none
Silene cobalticola (67)	Cu, Co
Silene burchelli (67)	none
Pearsonia metallifera (68)	Ni, Cr
Pearsonia marginata (68)	none

Among the plant species with a high genotypic differentiation, some species may be useful as regional indicators, if their formerly wide distribution has decreased over a great time period (in Europe from the postglacial, in Africa from the pluvial time onwards) and the restricted (relict) populations have maintained themselves only on soils with a surplus of heavy metals or other extreme soil conditions. The most pronounced example is *Minuartia verna*, which occurs nowadays on non-mineralized soils only in the alpine zone of its alpine-arctic distribution, but it is restricted to metalliferous soils in the colline and montane zone of Europe, from England [2, 72], throughout Central and Western Europe [2] up to Northern Greece [4]. In its alpine-arctic area metal-sensitive and metal-resistant populations co-occur, so that the species alone is not useful as metal-biomonitor in these regions. A similar situation has been discussed for the majority of cuprophyte species in Central Africa and for serpentinophytes in Zimbabwe, the latter on normal soils in South Africa, e.g. *Cyphostemma humile*, *Indigofera williamsonii* and *Sutera brunnea* [68]. Due to their disjunct distribution area their present isolation on heavy metal soils compared to their main area may cause also a genetic isolation. The small population number may further enhance effects and stimulate the selection of distinctive morphological characters because the isolated heavy metals soils have a quite distinct microclimate in comparison to the surrounding woodlands.

A step further in the evolution of indicator species are those species, which are nowadays restricted to metalliferous soils without having relatives on non-mineralized soils. The evolution of these species may be explained as neo-endemics [7], but more obviously they may be palaeo-endemics. One of these palaeo-endemics in Europe is the zinc-violet, *Viola calaminaria*. It occurs in a blue-flowering and a yellow-flowering form, both separated by a distance of nearly 150 km. The blue zinc-violet is restricted to a small Pb – Zn vein at Blankenrode in Germany [2, 3]. At this sites it regularly interacts with *Viola arvensis*. Due to the strong selection pressure for heavy metal tolerance the blue zinc-violet has survived on the zinc-lead soil the hybrid does not [75]. In Central Africa a lot of claims have been made for endemic species growing on copper and cobalt outcrops in Shaba, e.g. *Acalypha* *cupricola*, *Ascolepsis metallorum*, *Becium katangense*, *Rendlia cupricola* and *Sporobulus stelliger* [30, 76]. The long development of the population without a radical disturbance by glaciation may have favored the evolution of these endemics. On the other hand, a thorough floristic investigation and biosystematic evaluation may give perhaps a more modified view, as demonstrated for *Becium homblei* in Zimbabwe [65].

4.3.4 Specific Indicator Vegetation

Once individual species have adapted to a surplus of heavy metals, they will interact and build up specific plant communities. The assemblage of all these metal resistant species on a metal-enriched site will be quite different from that of neighboring sites. The metal concentration is the overwhelming species-selecting factor, often associated with low amounts of major nutrients such as nitrogen and phosphorus [2]. A metal concentration gradient will develop between the metal outcrop and the non-metal enriched surroundings [2], sometimes modified by seepage as on the copper outcrop at Dolfrwynog [15]. The steepness of the metal gradient will be determined by the metal concentration in the vein, its distance to the rooting zone of the plant species involved, and the re-arrangement of the lithological metal gradient by biological transport and decomposition processes and by groundwater leaching from the ore body, sometimes resulting in a seepage zone at the periphery of the sub-outcropping mineralized bedrock. At high metal concentrations, the plant communities on the metal-enriched substrates will be strongly different from the non-mineralized surroundings. In naturally forested areas of Europe [49] as well as of Africa [2, 15], these "out of context" plant communities [15] are characterized by a lack of trees, because tree species are nearly all unable to resist high metal concentrations [2]. The natural background vegetation is replaced by a vegetation characterized by the above mentioned metal resistant genotypes of common species such as the grasses *Agrostis capillaris*, *Deschampsia flexuosa* and *Festuca ovina* in cool-temperate Europe [2], *Aristida congesta*, *Schmidtia pappaphoroides* and *Rhyncelytrum repens* in semi-arid Southern Africa [15, 77], or *Andropogon gayanus*, *Brachiaria serrata* and *Trachypogon spicatus* in semi-humid South Central Africa [2, 78]. In addition, local and regional specific metal indicator plants may accomplish this open vegetation. Such "anomalous" or "out of context" plant communities provide an excellent surface indication of mineralization. Remnants of this vegetation can even be very helpful in identifying moderately mineralized soils, when man has changed the natural vegetation as in the above-mentioned example of Dolfrwynog in Wales [15].

The heavy metal vegetation has been described and summarized by Ernst [2] and recently reviewed for Europe [44], and for South Central Africa [69, 76]. Due to the metal gradients from the vein to the non-mineralized surroundings there are also gradients in occurrence of species and in densities of their populations, both resulting in a vegetation zonation along an orebody [2, 15, 36]. As example, on a copper vein

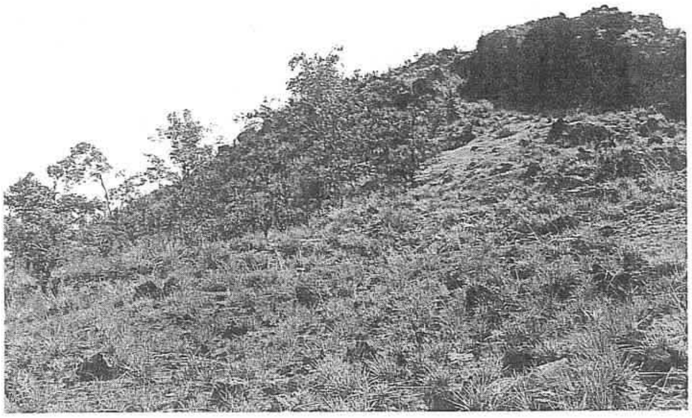

Fig. 3. A vegetation zonation caused by a copper gradient at Copper Queen, Zimbabwe. In front an open vegetation with the grasses *Danthoniopsis viridis* and *Chloridion cameronii* on highest copper values, followed by a zone with small shrubs and trees of *Vellozia equisetoides* and *Olax obtusifolia* and *Securidaca longepedunculata* on intermediate copper values.

in Namibia, the highly copper-enriched soil is indicated by a plant community with the typical indicator herb species *Helichrysum leptolepis* associated with *Mollugo cerviana* and *Barleria lanceolata* and the wide spread grasses *Aristida congesta* and *Eragrostis denudata*, followed by a less mineralized zone which is characterized by the absence of the above mentioned herbs and the presence of the *A. congesta*, *E. denudata* and additional *Anthephora pubescens*. The next zone is made up by the background savanna with *Acacia hereroensis*, *A. mellifera*, *Grewia flava*, *G. flavescens* and *G. bicolor* and the grass *Stipagrostis uniplumis* [15]. Such vegetation zonation is very site specific and modified not only by the metal concentration, but also by the genetic potential of the surrounding vegetation and by other soil factors such as nutrients, air humidity, soil moisture etc. [2] (Fig. 3).

Of course, a highly specialized vegetation on a soil poor in major nutrients will produce less biomass than background vegetation [2]. A consequence of these differences in productivity is the impact of plant litter on the changes of metal

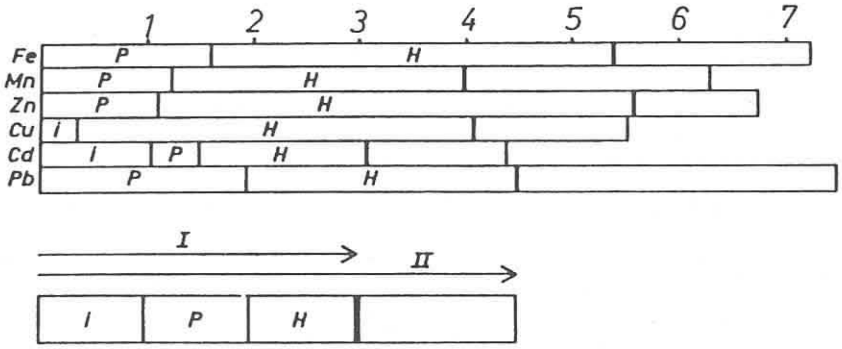

Fig. 4. Chemical forms of heavy metals of a metal outcrop at the Breiniger Berg (Germany), vegetated with a zinc-violet community with *Calluna vulgaris* [2]. I. water-soluble fraction with metals in (I) inorganic state, (P) complexed with phenolic acids and (H) complexed with humic compounds; II. HNO_3-soluble fraction [79].

speciation in such environmental gradients. Whereas on the bare or scarcely vegetated ore vein the heavy metals are present in an inorganic state, on the more vegetated part of the gradient they occur in various chemical forms, as ionic forms, or complexed with phenolic acids or humic compounds (Fig. 4, 79). Complexed metals are taken up by plants to a lesser degree than ionic metals; the speciation of metals will influence the plant species composition on metal enriched soils by facilitating less metal resistant species on soils with organically bound heavy metals [44].

4.3.5 Metal Vegetation in Europe

Within Europe the success of geobotanical prospecting is related to the combinations of metals in excess (the Pb – Zn – Cd, Cu – Zn, and Cu – Mn groups versus the Ni – Cr – Co groups) and to a climatic and vegetation-historical aspect. In the boreal and subarctic zone of Europe *Lychnis alpina* is a very worthful indicator accompanied by *Agrostis capillaris* and *Deschampsia flexuosa*: This species combination is found in Greenland [80], in Norway [49] and in Finland [44].

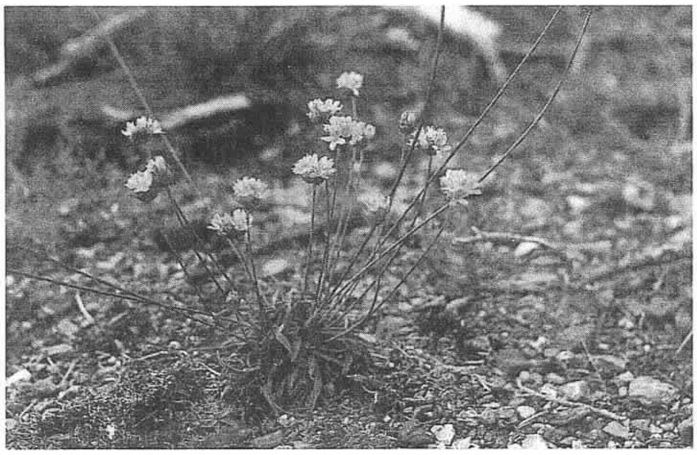

Fig. 5. *Armeria plantaginea* on a zinc-lead outcrop near Le Bleymard (France).

In the Atlantic zone of Europe *Silene vulgaris*, *Minuartia verna*, and *Thlaspi coerulescens* characterize zinc, lead and copper veins in the United Kingdom, West Germany, Belgium, France and the northern mountain zone of Spain [2], accomplished with regional indicators such as *Armeria maritima* s.l. in Spain, Wales, Belgium, and West Germany, *A. muelleri* in the Pyrenees, *A. plantaginea* in the Cevennes (Fig. 5), *Viola calaminaria* in Belgium and West Germany, *Viola lutea* in England. A very exceptional occurrence of *T. coerulescens* may be mentioned from a zinc-lead vein in Southern Sweden [81].

In Central Europe occurrences of a natural surplus of zinc, lead and copper are indicated by plant communities, characterized by *Minuartia verna*, *Silene vulgaris* and *Armeria halleri* (Fig. 6), or other endemic species of the genus *Armeria* [2].

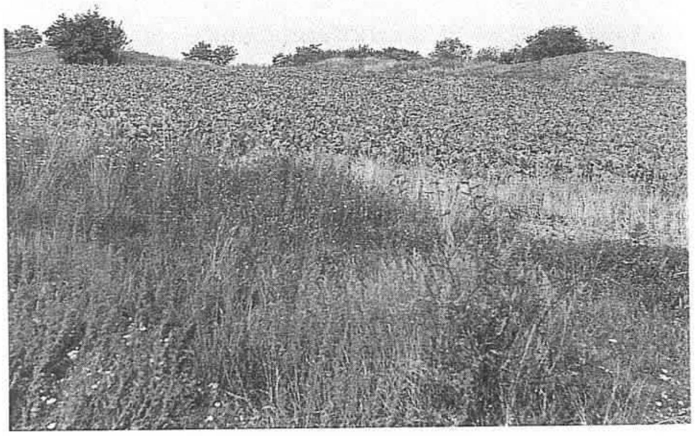

Fig. 6. A vegetation gradient with an *Armeria halleri* community on a zinc-copper outcrop surrounded by agricultural fields on metal-poor soil.

In the alpine zone of Europe *Minuartia verna* and *Silene vulgaris* co-occur with *Thlaspi rotundifolium* ssp. *cepaeifolium* or *Viola dubyana* (Fig. 7) on lead and zinc enriched soils. The alpine *T. rotundifolium* as well as the Atlantic *T. coerulescens* are both hyperaccumulators of zinc [2, 82]. On the Balkan peninsula *Minuartia verna* is a good indicator for zinc, copper and lead mineralization [2, 83], often associated with *Rumex acetosella*. The knowledge about the vegetation on these sites, however, is too incomplete for a final statement.

In the Mediterranean and Submediterranean zone of Europe areas with copper, lead and zinc mineralization are exploited for such a long time that the original vegetation has certainly disappeared completely or for a great deal, as it is obvious for the zinc veins of Lavrion in Greece [2, 47] and those of Cartagena in Spain [84].

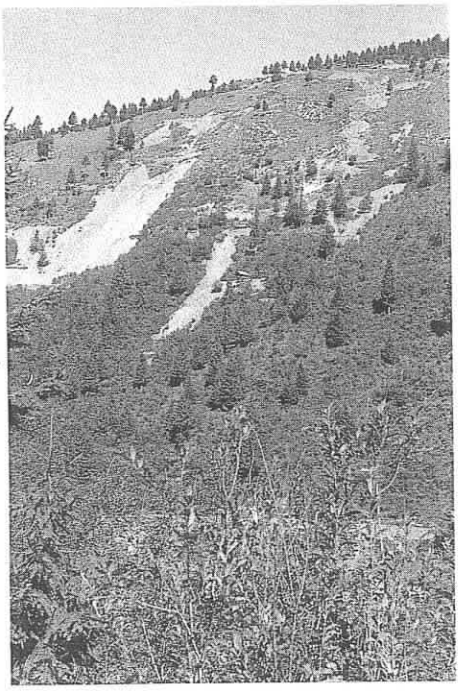

Fig. 7. A *Viola dubyana* grassland in the forested zone of the Piz Arera indicates a zinc-lead outcrop.

In contrast, areas with nickel minerals, often associated with serpentines, are only partly disturbed. Throughout Southern Europe, these sites are characterized by different *Alyssum* species being hyperaccumulators of nickel [2, 70].

4.3.6 Metal Vegetation in Africa

The relationship between vegetation and heavy metal veins in Africa is only partially known, the best from South Central Africa [2, 15, 69, 76, 78]. The less known situation is that of Northern Africa. Petit [31] has reported copper-resistant populations of *Rumex bucephalophorus* from Morocco, associated with plant taxa, which have shown the potential to develop metal resistance in Europe such as *Agrostis* and *Campanula* [2].

In West Africa the only report is concerned with a weak mineralization in the Nigerian lead-zinc belt [15]. Due to the relatively low plant-available metal concentration the species composition of the tree savanna is obviously not affected.

In South Central Africa a species combination with *Becium homblei*, *Eragrostis boehmii*, and *Loudetia simplex*, and with *Vellozia equisetoides* (Fig. 8) or other *Vellozia* species on rocky substrate, and *Dicoma niccolifera* on nickel-enriched serpentines, is very indicative for a surplus of copper and zinc in the soil [2, 24, 78]. The long lasting development of the Central African metal vegetation was undisturbed by glaciation or similar severe abiotic impacts, so that numerous local metalliferous endemics have developed resulting in highly species-specific plant communities on metal outcrops [2, 30, 76]. In the semi-arid parts of Southern Africa the indicator vegetation of heavy metal mineralization is characterized by *Helichrysum leptolepis*, which occur from Namibia [15] through Botswana to Transvaal [78]. An other indicator species is *Ecbolium lugardae*, but Wild [78] gives another taxonomic interpretation as Cole [15], so that a further taxonomic classificiation is demanded.

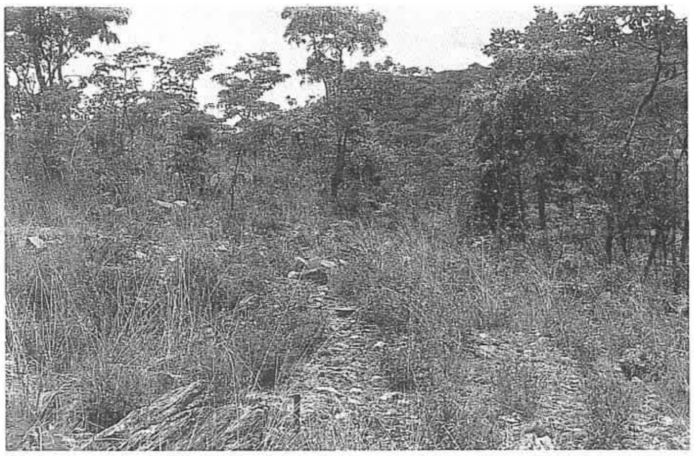

Fig. 8. A vegetation with *Becium homblei* in the copper outcrop surrounded by a savanna woodland with *Brachystegia boehmii* and *Julbernardia globiflora*.

4.4 References

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